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ANOMALOUS DEPENDENCE OF GLASS TEMPERATURE ON COMPOSITION OF BLOCK COPOLYMERS*

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A LARGE number of copolymers, including block copolymers, have been synthesized in recent times but there has been little study of their physical properties, particularly their glass temperatures (T_g) [1, 2]. There are practically no studies of this type on block copolymers. There are even fewer papers studying the transition temperatures of this class of polymer by nuclear magnetic resonance (NMR) and comparison of the results with those obtained by other methods. This problem is discussed in the present paper.

EXPERIMENTAL

The materials studied were polyurethane block copolymers [3], which can exist in the crystalline and amorphous states.

We studied *ortho*- and *para*-series of polyurethane block copolymers of the general formula

$$-(-\mathrm{A}-\mathrm{OCONHRNHCOO}-)_{100-n}-\ -(-\mathrm{B}-\mathrm{OCONHRNHCOO}-)_n-$$

where A is a block of the crystallizable aliphatic polyester polyethyleneglycoladipate (PEA), with the monomer unit $[-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CO}-(\mathrm{CH_2})_4-\mathrm{CO}-]$, B a block of crystallizable, arylene-containing polyester (PAA), namely poly-(bis-(β-hydroxyethoxy)phenylene adipate) $[-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-|\mathrm{C_6H_4}|_{1,4}^{1,3}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CO}-(\mathrm{CH_2})_4-\mathrm{CO}-]$, subsequently called *o*-PPA and *p*-PPA according to the points of attachment on the benzene ring, and on the molar percentage of B. The homopolymer containing blocks A, joined by urethane groups, will be called PEA-urethane and the corresponding homopolymers with block B *o*-PPA-urethane and *p*-PPA-urethane.

Each A block contains about ten and each B block about six monomer units. The molecular weights of all the samples were about 30,000. The melting points of the PEA-urethane and the *o*- and *p*-PPA-urethanes were 46, 72 and 148° respectively [3].

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